



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑪ Publication number:

**0 138 410**

**B1**

⑫

## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: **20.05.87** ⑯ Int. Cl.<sup>4</sup>: **C 11 D 3/40**  
⑯ Application number: **84306414.8**  
⑯ Date of filing: **19.09.84**

---

④ Process for the manufacture of coloured detergent powder.

---

⑯ Priority: **21.09.83 GB 8325326**

⑯ Proprietor: **UNILEVER PLC**  
Unilever House Blackfriars P.O. Box 68  
London EC4P 4BQ (GB)

⑯ Date of publication of application:  
**24.04.85 Bulletin 85/17**

⑯ GB

⑯ Publication of the grant of the patent:  
**20.05.87 Bulletin 87/21**

⑯ Proprietor: **UNILEVER NV**  
Burgemeester s'Jacobplein 1 P.O. Box 760  
NL-3000 DK Rotterdam (NL)

⑯ Designated Contracting States:  
**AT BE CH DE FR GB IT LI NL SE**

⑯ BE CH DE FR IT LI NL SE AT

⑯ References cited:  
**DE-A-2 257 163**  
**FR-A-2 262 085**  
**US-A-4 162 228**

⑯ Inventor: **Davies, Richard Llewellyn**  
59 Chorley Way Bebington  
Wirral Merseyside (GB)  
Inventor: **Don, Nigel Anderson**  
6 Tyburn Road Spital  
Bebington Merseyside L63 9HJ (GB)

**EP 0 138 410 B1**

⑯ Representative: **Mole, Peter Geoffrey et al**  
**UNILEVER PLC Patent Division P.O. Box 68**  
Unilever House Blackfriars  
London EC4P 4BQ (GB)

---

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

---

**Description**

This invention relates to a process for the manufacture of uniformly coloured detergent powder.

Coloured detergent powders are normally made by adding dye or pigment to a crutcher slurry and converting the slurry to a powder by spray-drying. Alternatively dye solution can be injected into the main feed to the nozzles of the spray-drying tower with similar results. The disadvantage of these processes is that they contaminate the whole of the spray-drying plant with colour so that when a white powder is subsequently to be made it is necessary to clean down, with consequent loss of production time.

One of the ways of avoiding this disadvantage is to spray a solution of dyestuff onto white powder. The main difficulty with this is that of contacting each individual particle, to an equal extent. If that is not achieved, then a speckled or mottled powder results.

United States Patent No. 4 162 228 relates to a method of colouring detergent flakes which contain nonionic surfactant as an essential component. The method involves mixing a dry colourant into the flakes whereupon the nonionic surfactant dissolves the colourant, imparting an overall hue to the flakes. Flakes are, of course, easier to colour than powder since they are translucent, and the whole formulation is contained within the flake. In contrast, powders normally consist of two components — a spray-dried portion and a dry-dosed portion which may have different affinities for colourant resulting in the powder having a mottled appearance.

GB-A-1 375 108 (Procter & Gamble) discloses a process for manufacturing a granular detergent composition containing a water-soluble blue dyestuff such as Polar Brilliant Blue or Ultramarine Blue yet which is substantially uncoloured in the dry state. The composition is prepared by mixing the dyestuff in dry form with a detergent powder or a granular ingredient thereof, and then spraying it with a liquid agglomerating agent.

These prior art processes involving the mixing of a dry colourant with a powder or flake detergent composition or ingredient thereof have led to products which are either non-uniformly coloured or not coloured at all.

We have now discovered contrary to what would have been expected that uniformly coloured powder can be manufactured by simply mixing a particulate colourant with a detergent powder, if the particulate colourant comprises both a pigment (water-insoluble) and a dyestuff (water-soluble).

Accordingly, the present invention, provides a process for the manufacture of a uniformly coloured detergent powder which comprises admixing with a detergent powder a particulate colourant comprising a water-insoluble pigment and a water-soluble dyestuff.

If desirable or necessary, after the mixing step

the coloured powder may be sprayed with a small percentage, for example 1—5% by weight, of water or of an ethoxylated alcohol nonionic surfactant in liquid or molten form. This can help to accentuate the colouration.

When choosing the colourant system it is important to select substances which will colour the powder adequately and yet not produce staining problems in the wash. We have found a combination of the pigment Ultramarine Blue, the dyestuff Duasyn® Acid Blue and the blue-whitener Polar Brilliant Blue to give excellent results on all types of detergent powder.

Other dyestuffs which have been found to be satisfactory are Carbolan®Violet, Gulf Acid Blue 6JS0 and Milling Blue 2BR, all of which are available from Imperial Chemical Industries Limited.

Preferably the mean particle size of the colourant is 0.5 to 5  $\mu\text{m}$ , most preferably about 2  $\mu\text{m}$ .

The process may be applied to powder which has been prepared by spray-drying, spray-cooling, granulation or agglomeration or any combination of these techniques. Additionally, any of the powder so produced may be dosed with conventional detergent powder additives such as sodium perborate tetrahydrate without altering the effectiveness of the process.

The apparatus used for mixing the particulate colourant and the powder is not critical to the process. We have found a rotating drum mixer to be perfectly satisfactory and also, a Patterson-Kelley (Registered Trade mark) batch blender has performed well.

The invention will be further described in the following example.

**Example**

White, spray-dried detergent powder is first fed down a chute at a flow rate of about 350 Kg/hour controlled by a slide valve into one end of the interior of a rotatable drum mixer without internal baffles. The axis of the drum mixer is approximately horizontal but the mean residence time of the powder in the drum which is about 2 minutes can be adjusted to some extent by moving the axis up or down by a few degrees. The drum is rotated and a finely powdered mixture of the following colourants is fed into the drum from a variable speed dosing unit:

	<u>% by weight</u>
55 Ultramarine Blue (pigment)	0.0800
60 Duasyn® Acid Blue (dyestuff)	0.0016
60 Polar Brilliant Blue (blue-whitener)	0.0020

Substantially uniformly blue coloured powder emerges from the discharge end of the drum mixer.

If desired the small quantity of water or nonionic surfactant referred to above, say 1—3% by weight may be sprayed onto the powder in the drum through spray nozzles located along the axis.

There are several advantages to the process described above. Most importantly it avoids colouration of the spray-drying plant, but also it appears to be independent of formulation, and is suitable for colouring fully-formulated powder and not just the spray-dried portion.

### Claims

1. A process for the manufacture of a uniformly coloured detergent powder, characterised in that there is admixed with a detergent powder a particulate colourant comprising a water-insoluble pigment and a water-soluble dyestuff.

2. A process as claimed in claim 1, characterised in that the particulate colourant comprises the blue pigment Ultramarine Blue and a dyestuff selected from Duasyn® Acid Blue, Carbolan® Violet, Gulf Acid Blue 6 JSO and Milling Blue 2BR.

3. A process according to claim 1 or claim 2, characterised in that the coloured powder is sprayed with from 1 to 5% by weight of water.

4. A process according to claim 1 or claim 2, characterised in that the coloured powder is sprayed with from 1 to 5% by weight of an ethoxylated alcohol nonionic surfactant in liquid or molten form.

5. A process according to any one of the preceding claims characterised in that the mean particle size of the colourant is from 0.5 to 5 µm.

6. A process according to claim 5, characterised in that the mean particle size of the colourant is about 2 µm.

### Patentansprüche

1. Verfahren zur Herstellung eines einheitlich gefärbten Detergentspulvers, dadurch gekennzeichnet, daß zu einem Detergentspulver ein teilchenförmiges Färbemittel, das ein wasserunlösliches Pigment und einen wasserlöslichen Farbstoff umfaßt, zugemischt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das teilchenförmige Färbemittel das

blaue Pigment Ultra-marinblau und einen Farbstoff ausgewählt unter Duasyn® Acid Blue, Carbolan® Violet, Gulf Acid Blue 6 JSO und Milling Blue 2BR umfaßt.

5. 3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das gefärbte Pulver mit 1 bis 5 Gew.-% Wasser besprüht wird.

10 4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das gefärbte Pulver besprüht wird mit 1 bis 5 Gew.-% eines ethoxylierten Alkohol-nonionic-Tesids in flüssiger oder geschmolzener Form.

15 5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die mittlere Partikelgröße des Färbemittels von 0,5 bis 5 µm beträgt.

20 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die mittlere Partikelgröße des Färbemittels etwa 2 µm beträgt.

### Revendications

25 1. Procédé de fabrication d'une poudre détergente uniformément colorée, caractérisé en ce qu'on mélange avec une poudre détergente un colorant particulaire comprenant un pigment insoluble dans l'eau et un colorant soluble dans l'eau.

30 2. Procédé selon la revendication 1, caractérisé en ce que le colorant particulaire comprend le pigment bleu Bleu Outremer et un colorant choisi parmi le Bleu Acide Duasyn (marque déposée), le Violet Carbolan (marque déposée), le Bleu Acide Gulf 6 JSO et le Bleu de Broyage 2BR.

35 3. Procédé selon la revendication 1 ou 2, caractérisé en ce qu'on pulvérise sur la poudre colorée de 1 à 5% en poids d'eau.

40 4. Procédé selon la revendication 1 ou 2, caractérisé en ce qu'on pulvérise sur la poudre colorée de 1 à 5% en poids d'un surfactif non ionique à base d'alcool éthoxylé sous forme liquide ou fondu.

45 5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la granulométrie moyenne du colorant est de 0,5 à 5 µm.

50 6. Procédé selon la revendication 5, caractérisé en ce que la grosseur moyenne des particules du colorant est d'environ 2 µm.



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑪ Publication number:

0 304 410  
A2

⑫

## EUROPEAN PATENT APPLICATION

⑯ Application number: 88870136.4

⑮ Int. Cl.<sup>4</sup>: C 11 D 3/40  
C 11 D 1/62, C 11 D 1/58

⑯ Date of filing: 16.08.88

⑯ Priority: 17.08.87 US 86117 30.06.88 US 213660

⑯ Applicant: THE PROCTER & GAMBLE COMPANY  
One Procter & Gamble Plaza  
Cincinnati Ohio 45202 (US)

⑯ Date of publication of application:  
22.02.89 Bulletin 89/08

⑯ Inventor: Wahl, Errol Hoffmann  
8021 Deershadow Lane  
Cincinnati Ohio 45242 (US)

⑯ Designated Contracting States:  
AT BE CH DE FR GB GR IT LI LU NL SE

Vimba, Alvars Ivars  
1135 Fuhrman Road  
Reading Ohio 45215 (US)

⑯ Representative: Canonici, Jean-Jacques et al  
Procter & Gamble European Technical Center N.V.  
Temselaan 100  
B-1820 Strombeek-Bever (BE)

⑯ Liquid fabric softener.

⑯ Liquid fabric softening compositions for use in a rinse bath  
after washing fabrics with a detergent. The softening compositions  
have a pH of less than about 7 and contain certain specific  
light-stable dyes at levels which provide a pink color.

EP 0 304 410 A2

## Description

## LIQUID FABRIC SOFTENER

5

TECHNICAL FIELD

10 This invention relates to compositions and methods for softening fabrics during the rinse cycle of home laundering operations. This is a widely used practice to impart to laundered fabrics a texture or hand that is smooth, pliable and fluffy to the touch (i.e., soft).

15 Liquid fabric softening compositions have long been known in the art and are widely utilized by consumers during the rinse cycles of automatic laundry operations. The term "fabric softening" as used herein and as known in the art refers to a process whereby a desirably soft hand and fluffy appearance are imparted to fabrics.

15

BACKGROUND ART

20 Compositions containing cationic nitrogenous compounds in the form of quaternary ammonium salts and substituted imidazolinium salts having two long chain acyclic aliphatic hydrocarbon groups are commonly used to provide fabric softening benefits when used in laundry rinse operations (See, for example, U.S. Pat. Nos. 3,644,203, Lamberti et al., issued Feb. 22, 1972; and 4,426,299, Verbruggen, Issued Jan. 17, 1984; also "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemists' 25 Society, January 1978, pages 118-121; and "How to Choose Cationics for Fabric Softeners," J. A. Ackerman, Journal of the American Oil Chemists' Society, June 1983, pages 1166-1169).

25 Quaternary ammonium salt having only one long chain acyclic aliphatic hydrocarbon group (such as monostearyltrimethyl ammonium chloride) are less commonly used because for the same chain length, compounds with two long alkyl chains were found to provide better softening performance than those having one long alkyl chain. (See, for example, "Cationic Fabric Softeners," W. P. Evans, Industry and Chemistry, July 30 1969, pages 893-903). U.S. Pat. No. 4,464,272, Parslow et al., issued Aug. 7, 1984, also teaches that monoalkyl quaternary ammonium compounds are less effective softeners.

30 Another class of nitrogenous materials that are sometimes used in fabric softening compositions are the nonquaternary amide-amines. A commonly cited material is the reaction product of higher fatty acids with hydroxy alkyl alkylene diamines. An example of these materials is the reaction product of higher fatty acids and hydroxyethylmethylenediamine (See "Condensation Products from  $\beta$ -Hydroxyethylmethylenediamine and Fatty Acids or Their Alkyl Esters and Their Application as Textile Softeners in Washing Agents," H. W. Eckert. Fette-Seifen-Anstrichmittel, September 1972, pages 527-533). These materials are usually cited generically along with other cationic quaternary ammonium salts and imidazolinium salts as softening actives in fabric softening compositions. (See U.S. Pat. Nos. 4,460,485, Rapisarda et al., issued July 17, 1984; 4,421,792, Rudy et al., issued Dec. 20, 1983; 4,327,133, Rudy et al., issued April 27, 1982). U.S. Pat. No. 3,775,316, Berg et al., issued Nov. 27, 1973, discloses a softening finishing composition for washed laundry containing (a) the condensation product of hydroxyalkyl alkylpolyamine and fatty acids and (b) a quaternary ammonium compound mixture of (i) from 0% to 100% of quaternary ammonium salts having two long chain alkyl groups and (ii) from 100% to 0% of a germicidal quaternary ammonium compound of the formula  $[R_5R_6R_7R_8N]^+$  A- 45 wherein  $R_5$  is a long chain alkyl group,  $R_6$  is a member selected from the group consisting of arylalkyl group and  $C_{12}$ - $C_{18}$  alkenyl and alkadienyl containing one or two  $C=C$  double bonds,  $R_7$  and  $R_8$  are  $C_1$ - $C_7$  alkyl groups, and A is an anion. U.S. Pat. No. 3,904,533, Neiditch et al., issued Sept. 9, 1975, teaches a fabric conditioning formulation containing a fabric softening compound and a low temperature stabilizing agent 50 which is a quaternary ammonium salt containing one to three short chain  $C_{10}$ - $C_{14}$  alkyl groups; the fabric softening compound is selected from a group consisting of quaternary ammonium salts containing two or more long chain alkyl groups, the reaction product of fatty acids and hydroxyalkyl alkylene diamine, and other cationic materials.

55

SUMMARY OF THE INVENTION

60 The present invention relates to fabric softening compositions in liquid form for use in home laundry operations. The present invention is based on the discovery that only a relatively few water-soluble dyes which are acceptable to consumers are capable of imparting a desirable pink color to such a product when the pH is lower than about 7, especially lower than about 4, especially in the presence of light.

According to the present invention, a fabric softening composition is provided in the form of an aqueous

dispersion comprising from about 3% to about 35% by weight of fabric softener, and from about 1 ppm to about 1,000 ppm, preferably from about 5 ppm to about 200 ppm of a dye system comprising a dye selected from the group consisting of: FD&C Red #4; FD&C Red #40; D&C Red #33; C.I. Acid Reds #'s 1, 18, and 395; C.I. Acid Violet #9; and mixtures thereof, the pH (10% solution) of the composition being less than about 7, preferably less than about 6.5, more preferably from about 3.0 to about 6.5, most preferably from about 3.0 to about 4. As used hereinafter, the FD&C and D&C #'s are all reds.

5

#### DETAILED DESCRIPTION OF THE INVENTION

10

The amount of fabric softening agent in the compositions of this invention is typically from about 3% to about 35%, preferably from about 4% to about 27%, by weight of the composition. The lower limits are amounts needed to contribute effective fabric softening performance when added to laundry rinse baths in the manner which is customary in home laundry practice. The higher limits are suitable for concentrated products which provide the consumer with more economical usage due to a reduction of packaging and distributing costs.

15

The preferred compositions are disclosed in U.S. Pat. No. 4,661,269, issued April 28, 1987, in the names of Toan Trinh, Errol H. Wahl, Donald M. Swartley and Ronald L. Hemingway, said patent being incorporated herein by reference.

20

#### The Composition

25

The fabric softening composition comprises the following components:

I. from about 3% to about 35%, preferably from about 4% to about 27%, by weight of the total composition of a fabric softener, and from about 1 ppm to about 1,000 ppm, preferably from about 5 ppm to about 200 ppm of a dye system comprising a visible amount of a dye selected from the group consisting of: FD&C #4; FD&C #40; D&C #33; C.I. Acid Reds #'s 1, 18, and 395; C.I. Acid Violet #9; and mixtures thereof, the pH (10% solution) of the composition being less than about 7, preferably less than about 6.5, more preferably from about 3.0 to about 6.5.

30

Preferably the fabric softener is a mixture comprising:

35

(a) from about 10% to about 92% of the reaction product of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof; (b) from about 8% to about 90% of cationic nitrogenous salts containing only one long chain acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon group; and optionally, (c) from 0% to about 80% of cationic nitrogenous salts having two or more long chain acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon groups or one said group and an arylalkyl group; said (a), (b) and (c) percentages being by weight of Component I; and

40

II. the balance of the composition comprising a liquid carrier selected from the group consisting of water and mixtures of the water and C<sub>1</sub>-C<sub>4</sub> monohydric alcohols.

As used herein, Component I comprises the mixture of fabric softening actives.

Following are the general descriptions of the essentials and optionals of the present compositions including a specific example. The example is provided herein for purposes of illustration only and is not intended to limit the claims, unless otherwise specified.

45

#### The Dyes

50

Water-soluble, nonstaining, light-stable dyes that are useful for creating a light-stable pink color are selected from the group consisting of: FD&C #4; FD&C #40; D&C Red #33; C.I. Acid Reds #'s 1, 18, and 395; C.I. Acid Violet #9; and mixtures thereof. The preferred dyes are C.I. Acid Red #1; C.I. Acid Red #18; and, if mixed with the other dyes, C.I. Acid Violet #9. C.I. Acid Violet #9 does not provide a very desirable pink color when used by itself. However, it is a good dye to blend with other dyes to provide a good pink color. In order to have a pink color, the level of dyes in the product has to be low, typically between about 1 ppm and about 1,000 ppm, preferably between about 5 ppm and about 200 ppm, most preferably between about 10 ppm and about 100 ppm. At these low levels, loss of even a small portion of the dye drastically changes the appearance. Accordingly, it is very important that the dyes not change color or lose color readily. Although D&C Red #19 has been used commercially, it is desirable to have alternates if safety considerations become important and for providing different shades of pink.

55

The listed dyes meet all of the requirements of these products.

60

Many "pink" dyes are unsuitable for one or more reasons. Furthermore, blue products have been preferred commercially. This may have reflected, in part, the difficulties in finding suitable dyes.

65

The preferred dye is Acid Red #1. A desirable dye system is a mixture of FD&C #40 with C.I. Acid Violet #9 at ratios of from about 0.2 to about 5. Many stable red dyes tend to have a "peach" appearance when used alone.

It is understood that equivalent dyes that are not certified, but that correspond chemically to the above certified dyes, are also included when the specific "certified" dyes are mentioned.

Some stable dyes like C.I. Acid Reds #'s 73 and 357 and C.I. Natural Red #8 provide color shades which are undesirable to consumers. FD&C Reds #'s 2 and 3, D&C Reds #'s 22 and 28, and C.I. Acid Reds #'s 14 and 51 proved unstable in sunlight. It is very difficult to find stable dyes that provide a truly acceptable, stable pink color.

10

## The Fabric Softeners

15 The preferred fabric softener of the invention comprises the following:

### Component 1(a)

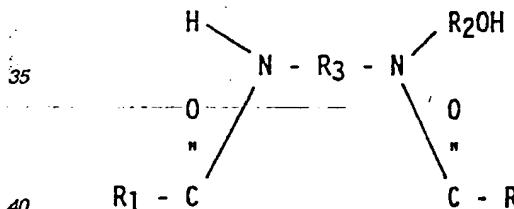
20

A preferred softening (active) of the present invention is the reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multifunctional structure of the polyamines (see, for example, the publication by H.W. Eckert in *Fette-Seifen-Anstrichmittel*, cited above).

25

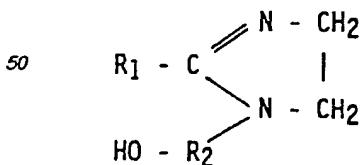
The preferred Component I(a) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures. More specifically, the preferred Component I(a) is compounds selected from the group consisting of:

(i) the reaction product of higher fatty acids with hydroxyalkylalkylenediamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



wherein R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>21</sub> hydrocarbon group and R<sub>2</sub> and R<sub>3</sub> are divalent C<sub>1</sub>-C<sub>3</sub> alkylene groups;

45 (ii) substituted imidazoline compounds having the formula:

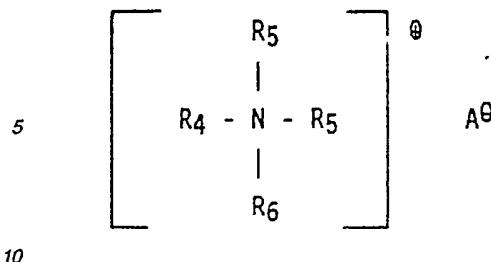


wherein  $R_1$  and  $R_2$  are defined as above:

(iii) substituted imidazoline compounds having the formula:

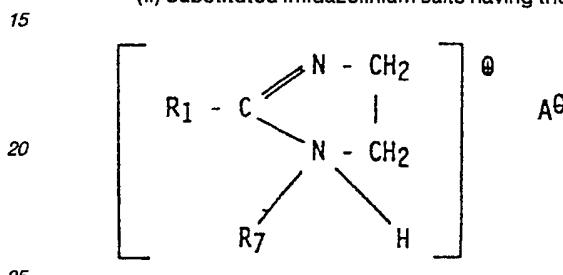
60

65



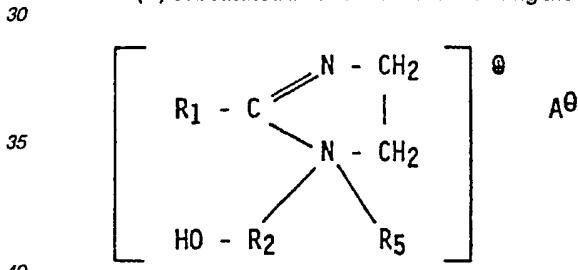
wherein  $R_4$  is an acyclic aliphatic C<sub>15</sub>-C<sub>22</sub> hydrocarbon group,  $R_5$  and  $R_6$  are C<sub>1</sub>-C<sub>4</sub> saturated alkyl or hydroxylalkyl groups, and  $A^\theta$  is an anion;

(ii) substituted imidazolinium salts having the formula:



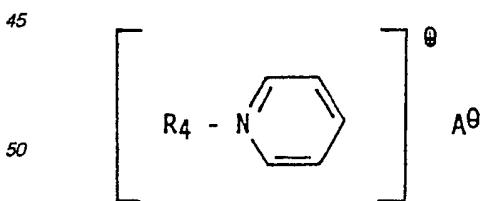
wherein  $R_1$  is an acyclic aliphatic C<sub>15</sub>-C<sub>21</sub> hydrocarbon group,  $R_7$  is a hydrogen or a C<sub>1</sub>-C<sub>4</sub> saturated alkyl or hydroxylalkyl group, and  $A^\theta$  is an anion;

(iii) substituted imidazolinium salts having the formula:



wherein  $R_2$  is a divalent C<sub>1</sub>-C<sub>3</sub> alkylene group and  $R_1$ ,  $R_5$  and  $A^\theta$  are as defined above;

(iv) alkylpyridinium salts having the formula:

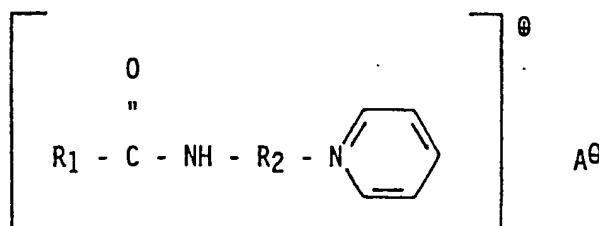


55 wherein  $R_4$  is an acyclic aliphatic C<sub>16</sub>-C<sub>22</sub> hydrocarbon group and  $A^\theta$  is an anion; and

(v) alkanamide alkylene pyridinium salts having the formula:

60

65



wherein  $\text{R}_1$  is an acyclic aliphatic  $\text{C}_{15}$ - $\text{C}_{21}$  hydrocarbon group,  $\text{R}_2$  is a divalent  $\text{C}_{1-3}$  alkylene group, and  $\text{A}^\theta$  is an ion group; and mixtures thereof.

Examples of Component I(b)(i) are the monoalkyltrimethylammonium salts such as monotallowtrimethylammonium chloride, mono(hydrogenated tallow)trimethylammonium chloride, palmityltrimethylammonium chloride and soyatrimethylammonium chloride, sold by Sherex Chemical Company under the trade names Adogen® 471, Adogen 441, Adogen 444, and Adogen 415, respectively. In these salts,  $\text{R}_4$  is an acyclic aliphatic  $\text{C}_{16}$ - $\text{C}_{18}$  hydrocarbon group, and  $\text{R}_5$  and  $\text{R}_6$  are methyl groups. Mono(hydrogenated tallow)trimethylammonium chloride and monotallowtrimethylammonium chloride are preferred. Other examples of Component I(b)(i) are behenyltrimethylammonium chloride wherein  $\text{R}_4$  is a  $\text{C}_{22}$  hydrocarbon group and sold under the trade name Kemamine® Q2803-C by Humko Chemical Division of Witco Chemical Corporation; soyadimethylethylammonium ethosulfate wherein  $\text{R}_4$  is a  $\text{C}_{16}$ - $\text{C}_{18}$  hydrocarbon group,  $\text{R}_5$  is a methyl group,  $\text{R}_6$  is an ethyl group, and  $\text{A}$  is an ethylsulfate anion, sold under the trade name Jordquat® 1033 by Jordan Chemical Company; and methyl-bis(2-hydroxyethyl)octadecylammonium chloride wherein  $\text{R}_4$  is a  $\text{C}_{18}$  hydrocarbon group,  $\text{R}_5$  is a 2-hydroxyethyl group and  $\text{R}_6$  is a methyl group and available under the trade name Ethoquad® 18/12 from Armak Company.

An example of Component I(b)(iii) is 1-ethyl-1-(2-hydroxyethyl)-2-isoheptadecylimidazolinium ethylsulfate wherein  $\text{R}_1$  is a  $\text{C}_{17}$  hydrocarbon group,  $\text{R}_2$  is an ethylene group,  $\text{R}_6$  is an ethyl group, and  $\text{A}$  is an ethylsulfate anion. It is available from Mona Industries, Inc., under the trade name Monaquat® ISIES.

A preferred composition contains Component I(a) at a level of from about 50% to about 90% by weight of Component I and Component I(b) at a level of from about 10% to about 50% by weight of Component I.

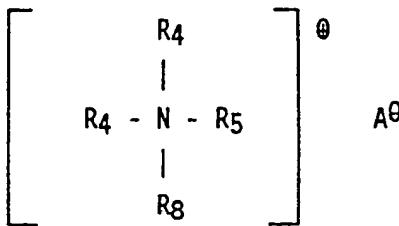
Cationic Nitrogenous Salts I(c)

35

Preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic  $\text{C}_{15}$ - $\text{C}_{22}$  hydrocarbon groups or one said group and an arylalkyl group are selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:

40



45

50

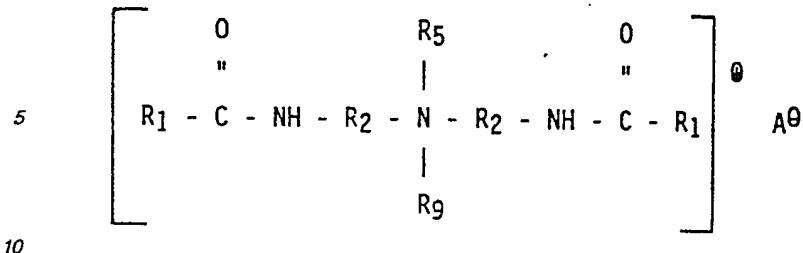
wherein  $\text{R}_4$  is an acyclic aliphatic  $\text{C}_{15}$ - $\text{C}_{22}$  hydrocarbon group,  $\text{R}_5$  is a  $\text{C}_1$ - $\text{C}_4$  saturated alkyl or hydroxalkyl group,  $\text{R}_8$  is selected from the group consisting of  $\text{R}_4$  and  $\text{R}_5$  groups, and  $\text{A}^\theta$  is an anion defined as above;

(ii) diamido quaternary ammonium salts having the formula:

55

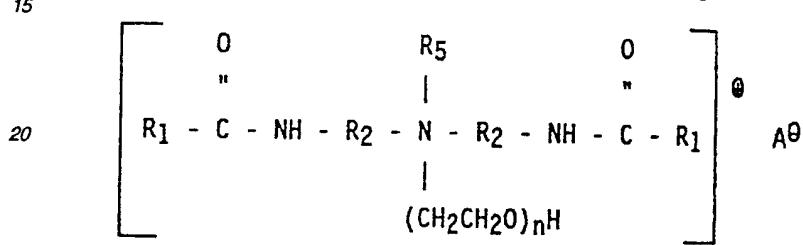
60

65



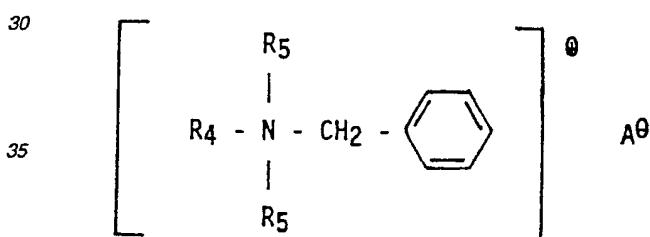
wherein  $\text{R}_1$  is an acyclic aliphatic  $\text{C}_{15}\text{-C}_{21}$  hydrocarbon group,  $\text{R}_2$  is a divalent alkylene group having 1 to 3 carbon atoms,  $\text{R}_5$  and  $\text{R}_9$  are  $\text{C}_1\text{-C}_4$  saturated alkyl or hydroxyalkyl groups, and  $\text{A}^\theta$  is an anion;

(iii) diamino alkoxylated quaternary ammonium salts having the formula:



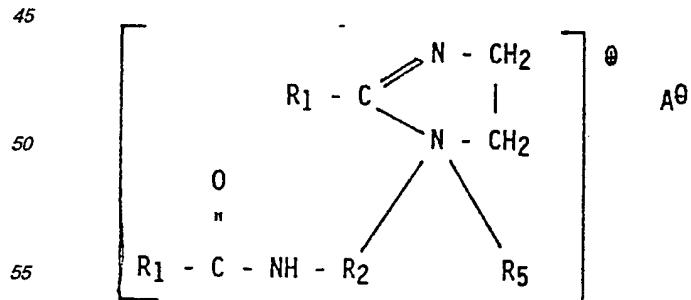
wherein  $n$  is equal to 1 to about 5, and  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_5$  and  $\text{A}^\theta$  are as defined above;

(iv) quaternary ammonium compounds having the formula:



wherein  $\text{R}_4$  is an acyclic aliphatic  $\text{C}_{15}\text{-C}_{22}$  hydrocarbon group,  $\text{R}_5$  is a  $\text{C}_1\text{-C}_4$  saturated alkyl or hydroxyalkyl group,  $\text{A}^\theta$  is an anion;

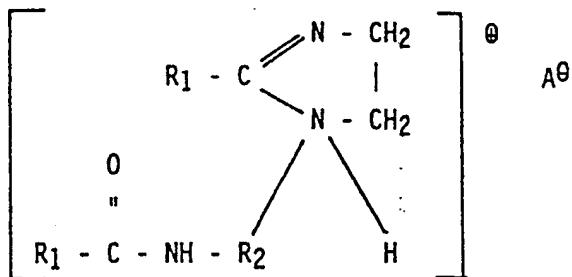
(v) substituted imidazolinium salts having the formula:



60

wherein  $\text{R}_1$  is an acyclic aliphatic  $\text{C}_{15}\text{-C}_{21}$  hydrocarbon group,  $\text{R}_2$  is a divalent alkylene group having 1 to 3 carbon atoms, and  $\text{R}_5$  and  $\text{A}^\theta$  are as defined above; and

(vi) substituted imidazolinium salts having the formula:



5

10

15

20

25

30

35

40

45

50

55

60

65

wherein R<sub>1</sub>, R<sub>2</sub> and A<sup>θ</sup> are as defined above; and mixtures thereof.

Examples of Component I(c)(i) are the well-known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenated tallow)dimethylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenated tallow)dimethylammonium chloride and ditallowdimethylammonium chloride are preferred. Examples of commercially available dialkyldimethylammonium salts usable in the present invention are di(hydrogenated tallow)dimethylammonium chloride (trade name Adogen 442), ditallowdimethylammonium chloride (trade name Adogen 470), distearyldimethylammonium chloride (trade name Arosurf<sup>®</sup> TA-100), all available from Shrex Chemical Company. Dibehenyldimethylammonium chloride wherein R<sub>4</sub> is an acyclic aliphatic C<sub>22</sub> hydrocarbon group is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation.

Examples of Component I(c)(ii) are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate wherein R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>17</sub> hydrocarbon group, R<sub>2</sub> is an ethylene group, R<sub>5</sub> is a methyl group, R<sub>6</sub> is a hydroxalkyl group and A is a methylsulfate anion; these materials are available from Shrex Chemical Company under the trade names Varisoft 222 and Varisoft 110, respectively.

An example of Component I(c)(iv) is dimethylstearylbenzylammonium chloride wherein R<sub>4</sub> is an acyclic aliphatic C<sub>18</sub> hydrocarbon group, R<sub>5</sub> is a methyl group and A is a chloride anion, and is sold under the trade names Varisoft SDC by Shrex Chemical Company and Ammonyx<sup>®</sup> 490 by Onyx Chemical Company.

Examples of Component I(c)(v) are 1-methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate and 1-methyl-1-(hydrogenated tallowamidoethyl)-2-(hydrogenated tallow)imidazolinium methylsulfate wherein R<sub>1</sub> is an acyclic aliphatic C<sub>15</sub>-C<sub>17</sub> hydrocarbon group, R<sub>2</sub> is an ethylene group, R<sub>5</sub> is a methyl group and A is a chloride anion; they are sold under the trade names Varisoft 475 and Varisoft 445, respectively, by Shrex Chemical Company.

A preferred composition contains Component I(c) at a level of from about 10% to about 80% by weight of said Component I. A more preferred composition also contains Component I(c) which is selected from the group consisting of: (i) di(hydrogenated tallow)dimethylammonium chloride and (v) methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate; and mixtures thereof. A preferred combination of ranges for Component I(a) is from about 10% to about 80% and for Component I(b) from about 8% to about 40% by weight of Component I.

Where Component I(c) is present, Component I is preferably present at from about 40% to about 27% by weight of the total composition. More specifically, this composition is more preferred wherein Component I(a) is the reaction product of about 2 moles of hydrogenated tallow fatty acids with about 1 mole of N-2-hydroxyethylethylenediamine and is present at a level of from about 10% to about 70% by weight of Component I; and wherein Component I(b) is mono(hydrogenated tallow)trimethylammonium chloride present at a level of from about 8% to about 20% by weight of Component I; and wherein Component I(c) is selected from the group consisting of di(hydrogenated tallow)dimethylammonium chloride, ditallowdimethylammonium chloride and methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate, and mixtures thereof; said Component I(c) is present at a level of from about 20% to about 75% by weight of Component I; and wherein the weight ratio of said di(hydrogenated tallow)dimethylammonium chloride to said methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is from about 2:1 to about 6:1.

The above individual components can also be used individually, especially those of I(c).

#### Anion A

In the cationic nitrogenous salts herein, the anion A<sup>θ</sup> provides electrical neutrality. Most often, the anion used to provide electrical neutrality in these salts is a halide, such as fluoride, chloride, bromide, or iodide. However, other anions can be used, such as methylsulfate, ethylsulfate, hydroxide, acetate, formate, sulfate, carbonate, and the like. Chloride and methylsulfate are preferred herein as anion A.

Other fabric softeners that can be used herein, typically in combination with the preferred fabric softener are disclosed in U.S. Pat. Nos. 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersema and Rieke; and 4,237,016, Rudkin, Clint, and Young, all of said patents being incorporated herein by reference.

5

Liquid Carrier

10 The liquid carrier is selected from the group consisting of water and mixtures of the water and short chain C<sub>1</sub>-C<sub>4</sub> monohydric alcohols. Water used can be distilled, deionized, or tap water. Mixtures of water and up to about 15% of a short chain alcohol such as ethanol, propanol, isopropanol or butanol, and mixtures thereof, are also useful as the carrier liquid.

15

Optional Ingredients

20 Adjuvants can be added to the compositions herein for their known purposes. Such adjuvants include, but are not limited to, viscosity control agents, perfumes, emulsifiers, preservatives, antioxidants, bacteriocides, fungicides, brighteners, opacifiers, freeze-thaw control agents, shrinkage control agents, and agents to provide ease of ironing. These adjuvants, if used, are added at their usual levels, generally each of up to about 5% by weight of the composition.

25 Viscosity control agents can be organic or inorganic in nature. Examples of organic viscosity modifiers are fatty acids and esters, fatty alcohols, and water-miscible solvents such as short chain alcohols. Examples of inorganic viscosity control agents are water-soluble ionizable salts. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. Calcium chloride is preferred. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 6,000 parts per million (ppm), preferably from about 20 to about 4,000 ppm by weight of the composition.

30 35 Examples of bacteriocides used in the compositions of this invention are glutaraldehyde, formaldehyde, 2-bromo-2-nitropropane-1,3-diol sold by Inolex Chemicals under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon® CG/ICP. Typical levels of bacteriocides used in the present compositions are from about 1 to about 1,000 ppm by weight of the composition.

40 45 Examples of antioxidants that can be added to the compositions of this invention are propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1, and butylated hydroxy toluene, available from UOP Process Division under the trade name Sustane® BHT.

The present compositions may contain silicones to provide additional benefits such as ease of ironing and improved fabric feel. The preferred silicones are polydimethylsiloxanes of viscosity of from about 100 centistokes (cs) to about 100,000 cs, preferably from about 200 cs to about 60,000 cs. These silicones can be used as is, or can be conveniently added to the softener compositions in a premulsified form which is obtainable directly from the suppliers. Examples of these premulsified silicones are 60% emulsion of polydimethylsiloxane (350 cs) sold by Dow Corning Corporation under the trade name DOW CORNING® 1157 Fluid and 50% emulsion of polydimethylsiloxane (10,000 cs) sold by General Electric Company under the trade name General Electric® SM 2140 Silicones. The optional silicone component can be used in an amount of from about 0.1% to about 6% by weight of the composition.

50 55 Soil release agents, usually polymers, are desirable additives at levels of from about 0.1% to about 5%. Suitable soil release agents are disclosed in U.S. Pat. Nos. 4,702,857, Gosselink, issued Oct. 27, 1987; 4,711,730, Gosselink and Diehl, issued Dec. 8, 1987; 4,713,194, Gosselink issued Dec. 15, 1987; and mixtures thereof, said patents being incorporated herein by reference. Other soil release polymers are disclosed in U.S. Pat. No. 4,749,596, Evans, Huntington, Stewart, Wolf, and Zimmerer, issued June 7, 1988, said patent being incorporated herein by reference.

60 Other minor components include short chain alcohols such as ethanol and isopropanol which are present in the commercially available quaternary ammonium compounds used in the preparation of the present compositions. The short chain alcohols are normally present at from about 1% to about 10% by weight of the composition.

65 A preferred composition contains from about 0.2% to about 2% of perfume, from 0% to about 3% of polydimethylsiloxane, from 0% to about 0.4% of calcium chloride, from about 1 ppm to about 1,000 ppm of bactericide, from about 10 ppm to about 100 ppm of dye, and from 0% to about 10% of short chain alcohols, by weight of the total composition.

The pH (10% solution) of the compositions of this invention is generally adjusted to be in the range of from about 3 to about 7, preferably from about 3.0 to about 6.5, more preferably from about 3.0 to about 4. Adjustment of pH is normally carried out by including a small quantity of free acid in the formulation. Because no strong pH buffers are present, only small amounts of acid are required. Any acidic material can be used; its selection can be made by anyone skilled in the softener arts on the basis of cost, availability, safety, etc. Among the acids that can be used are hydrochloric, sulfuric, phosphoric, citric, maleic, and succinic. For the purposes of this invention, pH is measured by a glass electrode in a 10% solution in water of the softening composition in comparison with a standard calomel reference electrode.

The liquid fabric softening compositions of the present invention can be prepared by conventional methods. A convenient and satisfactory method is to prepare the softening active premix at about 72°-77°C, which is then added with stirring to the hot water seat. Temperature-sensitive optional components can be added after the fabric softening composition is cooled to a lower temperature.

The liquid fabric softening compositions of this invention are used by adding to the rinse cycle of conventional home laundry operations. Generally, rinse water has a temperature of from about 5°C to about 60°C. The concentration of the fabric softener actives of this invention is generally from about 10 ppm to about 200 ppm, preferably from about 25 ppm to about 100 ppm, by weight of the aqueous rinsing bath.

In general, the present invention in its fabric softening method aspect comprises the steps of (1) washing fabrics in a conventional washing machine with a detergent composition; and (2) rinsing the fabrics in a bath which contains the abovedescribed amounts of the fabric softeners; and (3) drying the fabrics. When multiple rinses are used, the fabric softening composition is preferably added to the final rinse. Fabric drying can take place either in an automatic dryer or in the open air.

All percentages, ratios, and parts herein are by weight unless otherwise indicated.

5

10

15

20

25

30

35

40

45

50

55

60

65

## EP 0 304 410 A2

EXAMPLES

	<u>Ingredient</u>	<u>Wt.%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
5	Adogen® 448E-83HM <sup>1</sup>	7.96	7.97	7.97	4.54
	Varisoft® 445				
	Imidazoline <sup>2</sup>	6.21	6.21	6.21	3.40
10	Adogen® 441 <sup>3</sup>	0.97	0.97	0.97	0.57
	Polydimethyl Siloxane (55%)	0.61	0.61	0.61	0.32
	Silicone DC 1520 (20%)	0.015	0.015	0.015	0.015
15	Perfume	0.90	0.90	0.90	0.42
	Varonic® T 220 D	0.43	0.43	0.43	0.10
	Kathon®	0.034	0.034	0.034	0.034
20	Tenox® S-1	0.025	0.025	0.025	-
	Hydrochloric Acid (31.5%)	1.25	1.25	1.25	0.62
	Calcium Chloride				
25	25% Solution	1.10	1.10	1.10	0.003
	FD&C Red #40 (1%)	0.07	-	0.10	-
	D&C #19 (0.75%)	0.03	-	-	-
30	Acid Red #1 (1%)	-	0.15	-	0.10
	Acid Violet #9 (1%)	-	-	0.10	-
	Water	Balance	Balance	Balance	Balance

35           1 A mixture of ditallowalkyl dimethylammonium chloride and  
monotallowalkyl trimethylammonium chloride.

40           2 Di long chain (tallow) alkyl imidazolinium softener.

45           3 Monotallowalkyl trimethylammonium chloride.

50           The base product is made by a process that is similar to processes used for commercial products and the  
dyes are simply added to the finished product. Products with C.I. Acid Reds #'s 1, 18 and 395; C.I. Acid Violet  
#9, D&C Red #33, FD&C #4, and #40 are acceptably stable when exposed to sunlight for two days, and  
other dyes such as FD&C #2, FD&C #3, Acid Red #87, Acid Red #14, D&C #22, and D&C #28 were  
found to be unstable.

55

**Claims**

60

65           1. A fabric softening composition in the form of an aqueous dispersion comprising from about 3% to  
about 35% by weight of fabric softener and from about 1 ppm to about 1,000 ppm of a dye system which  
comprises a dye selected from the group consisting of FD&C Red #4; FD&C Red #40; D&C Red #33;  
C.I. Acid Red #1; C.I. Acid Red #18; C.I. Acid Red #395; C.I. Acid Violet #9; and mixtures thereof, the  
pH of a 10% solution of the composition being less than about 7.

2. The composition of Claim 1 wherein the pH is less than about 7 and the dye is present at a level of from about 5 ppm to about 200 ppm.
3. The composition of Claim 1 wherein the dye system comprises FD&C Red # 40.
4. The composition of Claim 1 wherein the dye system comprises FD&C Red # 4.
5. The composition of Claim 1 wherein the dye system comprises C.I. Acid Red #395. 5
6. The composition of Claim 1 wherein the dye system comprises C.I. Acid Red #1.
7. The composition of Claim 1 wherein the dye system comprises C.I. Acid Red #18.
8. The composition of Claim 1 wherein the pH of a 10 solution is from about 7 to about 3.0.
9. The composition of Claim 1 wherein the dye system comprises a mixture of D&C Red # 19 and FD&C Red # 40 in the ratio of from about 1:2 to about 1:9. 10
10. The composition of Claim 1 wherein the dye system comprises a mixture of FD&C Red # 40 and C.I. Acid Violet #9 in the ratio of from about 0.2 to about 5.

15

20

25

30

35

40

45

50

55

60

65



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 304 410  
A3

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 88870136.4

(51) Int. Cl. 5. C11D 3/40, C11D 1/62,  
C11D 1/58

(22) Date of filing: 16.08.88

(30) Priority: 17.08.87 US 86117  
30.06.88 US 213660

(71) Applicant: THE PROCTER & GAMBLE  
COMPANY  
One Procter & Gamble Plaza  
Cincinnati Ohio 45202(US)

(43) Date of publication of application:  
22.02.89 Bulletin 89/08

(72) Inventor: Wahl, Errol Hoffmann  
8021 Deershadow Lane  
Cincinnati Ohio 45242(US)  
Inventor: Vimba, Aivars Ivars  
1135 Fuhrman Road  
Reading Ohio 45215(US)

(84) Designated Contracting States:  
AT BE CH DE FR GB GR IT LI LU NL SE

(73) Representative: Canonici, Jean-Jacques et al  
Procter & Gamble European Technical  
Center N.V. Temselaan 100  
B-1820 Strombeek-Bever(BE)

(88) Date of deferred publication of the search report:  
18.07.90 Bulletin 90/29

(54) Liquid fabric softener.

(57) Liquid fabric softening compositions for use in a  
rinse bath after washing fabrics with a detergent.  
The softening compositions have a pH of less than  
about 7 and contain certain specific light-stable dyes  
at levels which provide a pink color.

EP 0 304 410 A3



EP 88 87 0136

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
A	EP-A-0199382 (THE PROCTER & GAMBLE COMPANY) * column 4, line 5 - column 21, line 14 *	1	C11D3/40 C11D1/62 C11D1/58						
D	& US-A-4611269								
A	EP-A-0005850 (HENKEL KGAA) * example 1 *	1							
A	US-A-3892669 (A.A. RAPISARDA) * column 8, lines 14 - 27; claim 1 *	1							
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)						
			C11D						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>15 MAY 1990</td> <td>TETAZ F.C.E.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	15 MAY 1990	TETAZ F.C.E.
Place of search	Date of completion of the search	Examiner							
THE HAGUE	15 MAY 1990	TETAZ F.C.E.							
<p>2</p> <p>EPO FORM 1501032 (P001)</p>		<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>							

THIS PAGE BLANK (USPTO)